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THE POLING FIELD AND DRAW DEPENDENCE OF THE PIEZOELECTRIC AND P--ETC(U)
JUL 81 J I SCHEINBEIM, K T CHUNG

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Recent investigations [1] have shown that unoriented phase I poly(vinylidene fluoride) (PVF₂) films can be produced by pressure quenching. The poling field dependence of the pyroelectric coefficient, P_y , the piezoelectric coefficients d_p , d_{31} , and e_{31} and the dielectric response is investigated for poling fields up to $E_p = 2.75 \times 10^6$ V/cm. These quantities exhibit a plateau region where the initial rapid increase with increasing E_p decreases. This behavior is similar to that observed for

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oriented phase II PVF₂ films. The effect of draw ratio on d_p and P_y for draw ratios up to 6:1 is also examined. d_p increases from 6.5 pC/N to 19 pC/N as the draw ratio goes from 1:1 to 6:1 (at constant E_p). P_y increases from 1×10^{-9} C/cm²K to 5×10^{-9} C/cm²K.

$\rightarrow 1 \times 10$ to the minus ninth power $C / 59 \text{ cm K}$
 to 5×10 to the minus ninth power $C / 59 \text{ cm K}$.

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THE POLING FIELD AND DRAW DEPENDENCE OF THE PIEZOELECTRIC
AND PYROELECTRIC RESPONSE OF PRESSURE QUENCHED PHASE I
POLY(VINYLDENE FLUORIDE) FILMS

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Abstract

Recent investigations⁽¹⁾ have shown that unoriented phase I poly(vinylidene fluoride) (PVF₂) films can be produced by pressure quenching. The poling field dependence of the pyroelectric coefficient, P_y , the piezoelectric coefficients d_p , d_{31} , and e_{31} and the dielectric response is investigated for poling fields up to $E_p = 2.75 \times 10^6$ V/cm. These quantities exhibit a plateau region where the initial rapid increase with increasing E_p decreases. This behavior is similar to that observed for unoriented and biaxially oriented phase II PVF₂ films. The effect of draw ratio on d_p and P_y for draw ratios up to 6:1 is also examined. d_p increases from 6.5 pC/N to 19 pC/N as the draw ratio goes from 1:1 to 6:1 (at constant E_p). P_y increases from 1×10^{-9} C/cm²K to 5×10^{-9} C/cm²K.

Introduction

In a previous study, Scheinbeim, Nakafuku, Newman, and Pae⁽¹⁾ investigated a new method for crystallizing poly(vinylidene fluoride) (PVF_2) in the phase I crystal form. This method involved melting PVF_2 at pressures ~ 1 Kbar and then rapidly bringing the molten polymer to a supercooled state by suddenly increasing the pressure to ~ 7 Kbar. The rapid (high pressure) quenching technique resulted in an unoriented sample containing the phase I form with no evidence of any sample degradation. High pressure isobaric melt-crystallization of PVF_2 above ~ 3.5 Kbar will also produce phase I; however, significant sample degradation occurs.

By varying the final (quenching) pressure, we were able to obtain unoriented PVF_2 films containing various percentages of the phase I and phase II crystal forms. Scheinbeim, Chung, Pae, and Newman⁽²⁾ then showed that the piezoelectric response (d_{31} and e_{31} , the piezoelectric strain and stress coefficients) increased linearly with increasing phase I content as long as the poling field was below the threshold field necessary to convert phase II to Phase IV. The crystallinity of these films was $\sim 55\%$ and was, surprisingly, independent of the crystallization pressure and temperature. This constancy of crystallinity has been previously observed for PVF_2 crystallized under various conditions at atmospheric pressure but is not well understood.

In the present study, we investigate the poling field (E_p) dependence of the piezoelectric and pyroelectric response of unoriented pressure quenched PVF_2 films containing only the phase I form. As E_p increases, a plateau region is observed in the piezoelectric and pyroelectric response similar to that observed by Newman, Yoon, Pae, and Scheinbeim⁽³⁾ for both unoriented and biaxially oriented phase II films. This plateau region, where the increase

in piezoelectric response with increasing poling field is quite small, was found to be associated with the completion of field-induced crystal structure transformation from phase II to more polar forms. However, in the present study, only the most polar phase I form is present and the plateau region appears to be related to changes in the mechanism of the field-induced re-orientation of phase I crystallites produced by chain rotation.

In addition, we were able to investigate the effect of film draw on the piezoelectric and pyroelectric response of films poled under identical conditions. Early studies in this area by Shuford, Wilde, Ricca, and Thomas⁽⁴⁾ and, recently, by McGrath and Ward⁽⁵⁾ examined the effects of draw on films which before drawing contain only the (unoriented) phase II form. When drawn under appropriate conditions, these films will convert to (oriented) phase I; however, the effect of film draw on subsequent piezoelectric or pyroelectric response is somewhat clouded by the occurrence of the crystal phase transition. In the present study we avoid this difficulty by using initially unoriented phase I films.

Experimental

Unoriented phase I PVF₂ films were prepared using the previously described pressure quenching technique^(1,2). Gold electrodes were evaporated on the un-oriented films which were then poled at different poling fields up to 2.75×10^6 V/cm for 1 hour. The poling temperature was 23°C and poling was performed under vacuum using a conventional poling technique^(2,3).

Samples used for the study of the draw dependence on the piezoelectric and pyroelectric response were drawn at 110°C and annealed under tension for

30 minutes at this temperature. The samples were electroded and poled as previously described. Drawing was done in small steps in a discontinuous manner. The rate of draw was not recorded.

Piezoelectric strain coefficient (d_{31}), piezoelectric stress coefficient (e_{31}), and dielectric constant measurements at 3 Hz were performed using a Toyo Seiki Piezotron. Pyroelectric measurements were obtained using a heating and cooling rate of 1.75°C/min. The pyroelectric coefficient (P_y) was calculated from:

$$P_y = \frac{1}{A} \left(\frac{I_+ - I_-}{2\beta} \right)$$

where I_+ and I_- are the currents obtained on heating and cooling cycles, respectively, β is the heating rate, and A is the electrode area. This procedure for determining P_y removes the small but significant contribution of thermally stimulated currents from the pyroelectric current. The hydrostatic piezoelectric coefficient (d_p) was determined by measuring changes in surface charge with incremental changes in pressure as previously described⁽⁶⁾.

Results and Discussion

The poling field dependence of the pyroelectric coefficient, P_y , is shown in Fig. 1. P_y increases rapidly with increasing poling field (E_p), exhibiting an almost linear increase with E_p between $0.5 - 2 \times 10^6$ V/cm and reaches a value of 1.46×10^{-9} C/cm²K at 2×10^6 V/cm. Between 2 and 2.5×10^6 V/cm, the rate of increase of P_y is quite small: this region is designated as the plateau region. Between 2.5 and 2.75×10^6 V/cm, P_y again exhibits a rapid rise reaching a value of 1.68×10^{-9} C/cm²K at 2.75×10^6 V/cm.

The poling field dependence of the hydrostatic piezoelectric coefficient, d_p ,

exhibits a similar behavior as shown in Fig. 2; however, the plateau region is not as sharply defined as is the case for P_y . It also appears that the onset of the plateau region for d_p begins at $\sim 10^6$ V/cm, a much lower value of E_p than for the onset of the plateau region for P_y . The plateau region for d_p ends at $\sim 2 \times 10^6$ V/cm and for $E_p > 2 \times 10^6$ V/cm, d_p again increases rapidly with increasing poling field, reaching a value of ~ 10 pC/N when $E_p = 2.75 \times 10^6$ V/cm.

The poling field dependence of the piezoelectric stress coefficient, e_{31} , and the piezoelectric strain coefficient, d_{31} , (measured at 3 Hz) also exhibit plateau behavior as shown in Figures 3 and 4, respectively. Both e_{31} and d_{31} show a small increase with increasing E_p up to 0.5×10^6 V/cm, followed by a rapid rise with increasing E_p up to $E_p = 10^6$ V/cm where the plateau region begins. The plateau region is much better defined for e_{31} than for d_{31} . The plateau region for d_{31} ends at $E_p = 2.5 \times 10^6$ V/cm and for $E_p = 2.75 \times 10^6$ V/cm, $d_{31} = 8$ pC/N. The plateau region for e_{31} ends at $\sim 2 \times 10^6$ V/cm and for $E_p = 2.75 \times 10^6$ V/cm, $e_{31} = 14.5$ mC/m².

Figure 5, a comparison of the poling field dependence of d_{31} for the unoriented phase I films, biaxially oriented phase II films (containing some phase I), and unoriented phase II films, shows that the plateau region is a common phenomena. This is also apparent in Figure 6, a comparison of the poling field dependence at e_{31} for the three types of films: All three types of films were prepared from the same roll of 25 micron Kureha capacitor grade film. For the phase II films, it was shown⁽³⁾ that the plateau region corresponds to the completion of the field-induced transformation of phase II to phase IV. For the unoriented phase I films, no crystal transformation to a more polar form is likely since phase I is the most polar form known. Wide angle x-ray diffraction scans of the unoriented phase I samples poled at

fields up to and including 2×10^6 V/cm are identical within experimental error, indicating that the poling mechanism is probably 180° switching of the molecular dipoles producing a 180° rotation of crystallites as previously suggested⁽²⁾. This would be consistent with the development of film polarization and the lack of change in the x-ray diffraction patterns. At poling field of 2.5×10^6 V/cm and higher, small but significant changes (increases in the (020) reflection) are observed. These changes would be consistent with the onset of another polarization mechanism, possibly the 60° switching proposed by Kepler and Anderson⁽⁷⁾.

Figure 7 shows the poling field dependence of the dielectric constant of the unoriented phase I film, measured at 3 Hz (23°C). The dielectric constant, ϵ' , of the unpoled film is 12 which decreases to ~ 11 in the plateau region which extends from $1-2 \times 10^6$ V/cm. At higher poling fields, ϵ' drops off rapidly reaching a value of 10 when $E_p = 2.75 \times 10^6$ V/cm. The reason for the observed decrease in ϵ' is not apparent but may be related to a decrease in the mobility of the molecular dipoles in the amorphous region. This could be produced by the effects of the large local fields produced by the field oriented polar crystallites or by strains produced in the amorphous regions caused by the field-induced reorientation of the chains in the crystallites. Measurements of the dielectric response through the glass transition region for these films may provide further information. This is part of a future study and no further speculation is warranted.

Figure 8 shows the effect of sample draw on the pyroelectric coefficient. Samples with draw ratios of 1:1, 3:1, 4:1, 5:1, and 6:1 were studied. P_y increases from a value of 1×10^{-9} C/cm²K for the undrawn film to a value of 5×10^{-9} C/cm²K for the sample with a 6:1 draw ratio. The shape of the curve

is similar to that obtained previously⁽⁴⁾ for the draw dependence of d_{31} for films initially containing unoriented phase II crystallites. Figure 9 shows the effect of draw on the hydrostatic piezoelectric coefficient, d_p , and also has a similar shape: d_p increases from a value of 6.5 pC/N to a value of 19 pC/N as the draw ratio goes from 1:1 to 6:1. Our results show that the most rapid increase in P_y and d_p occurs for draw ratios between 3:1 and 5:1. This also agrees with the earlier study; however, the earlier study showed that the maximum rate of draw induced transformation from unoriented phase II to oriented phase I occurred in this region. In the present study, no crystal phase transformation occurs and the transition is from unoriented phase I to oriented phase I. This suggests that at the draw temperature of 110°C, crystallite orientation occurs most rapidly for draw ratios between 3:1 and 5:1. This will be investigated in detail in future studies.

Conclusions

In this study, we have investigated the poling field dependence of the piezoelectric, pyroelectric, and dielectric response of unoriented, pressure quenched, phase I PVF₂ films. P_y , d_p , d_{31} , e_{31} , and ϵ' all exhibit a plateau region with increasing E_p similar to that previously observed for unoriented and biaxially oriented phase II PVF₂ films⁽³⁾. The plateau regions indicates that more than one polarization mechanism exists; possibly a field-induced 180° reorientation at lower fields (up to $E_p \approx 2 \times 10^6$ V/cm) followed by a 60° reorientation at higher fields ($E_p \geq 2.5 \times 10^6$ V/cm).

We have also investigated the draw dependence of P_y and d_p for unoriented phase I films drawn at 110°C. These curves are similar to that previously observed⁽⁴⁾ for the draw dependence of d_{31} for unoriented phase II films.

1.

The most rapid increase in d_p and P_y occurs for draw ratios between 3:1 and 5:1, indicating that the change in crystallite orientation is greatest in this region.

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Figure Captions

- Figure 1: - The poling field dependence of the pyroelectric response of un-oriented phase I PVF₂ films.
- Figure 2: - The poling field dependence of the hydrostatic piezoelectric coefficient, d_p , of unoriented phase I PVF₂ films.
- Figure 3: - The poling field dependence of the piezoelectric stress coefficient, e_{31} , of unoriented phase I PVF₂ films.
- Figure 4: - The poling field dependence of the piezoelectric strain coefficient, d_{31} , of unoriented phase I PVF₂ films.
- Figure 5: - A comparison of the poling field dependence of d_{31} for unoriented phase I, unoriented phase II, and biaxially oriented phase II PVF₂ films. All films poled at 23°C.
- Figure 6: - A comparison of the poling field dependence of e_{31} for unoriented phase I, unoriented phase II, and biaxially oriented phase II PVF₂ films. All films poled at 23°C.
- Figure 7: - The poling field dependence of the dielectric constant, ϵ' , of unoriented phase I PVF₂ films measured at 3 Hz and 23°C.
- Figure 8: - The draw ratio dependence of the pyroelectric response of PVF₂ films drawn at 110°C.
- Figure 9: - The draw ratio dependence of the hydrostatic piezoelectric coefficient of PVF₂ films drawn at 110°C.















